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Synthesis and characterization of $Na(Gd_{0.5}Lu_{0.5})F_4$: Nd^{3+},a core-shell free multifunctional contrast agent

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ABSTRACT

Compared to conventional core-shell structures, core-shell free nanoparticles with multiple functionalities offer several advantages such as minimal synthetic complexity and low production cost. In this paper, we present the synthesis and characterization of Nd^{3+} doped $Na(Gd_{0.5}Lu_{0.5})F_4$ as a core-shell free nanoparticle system with three functionalities. Nanocrystals with 20 nm diameter, high crystallinity and a narrow particle size distributions were synthesized by the solvothermal method and characterized by various analytical techniques to understand their phase and morphology. Fluorescence characteristics under near infrared (NIR) excitation at 808 nm as well as X-ray excitation were studied to explore their potential in NIR optical and X-ray imaging. At 1.0 mol% Nd concentration, we observed a quantum yield of 25% at 1064 nm emission with 13 W/cm^2 excitation power density which is sufficiently enough for imaging applications. Under 130 kVp (5 mA) power of X-ray excitation, Nd^{3+} doped $Na(Gd_{0.5}Lu_{0.5})F_4$ shows the characteristic emission bands of Gd^{3+} and Nd^{3+} with the strongest emission peak at 1064 nm due to Nd^{3+}. Furthermore, magnetization measurements show that the nanocrystals are paramagnetic in nature with a calculated magnetic moment per particle of ~570 μB at 2T. These preliminary results support the suitability of the present nanophosphor as a multimodal contrast agent with three imaging features viz. optical, magnetic and X-ray.

1. Introduction

Rare earth doped materials find several potential applications in several areas such as lasers, optical temperature sensors, white light-emitting diodes, and dye-sensitized solar cells [1–6]. With the introduction of nanotechnology there are so much interest in the development and applications of rare earth based multifunctional nanomaterials. One of the most important areas is biomedical imaging, where nanomaterials with multiple imaging features have been used as contrast agents [7–9]. Several imaging modalities, such as X-ray/computed tomography (CT), magnetic resonance imaging (MRI), and optical imaging, currently use contrast agents to improve cell and tissue images. The variation of each imaging modality offers a unique advantage in spatial resolution, imaging depth, sensitivity, and ease of use.

Several multimodal inorganic contrast agents with core-shell structures have been reported in the past. For example, core-shell quantum dots (QD) have been proposed as a suitable multimodal agent due to their unique optical properties such as multiplexing capabilities, photo-stability, and high fluorescence yield [10–14]. Coupling the QDs with the magnetic metal ion core can lead to a dual model contrast agent. However, there are several significant shortcomings with these imaging agents. QDs show several undesirable properties such as luminescence blinking, high toxicity, and requiring precise size tuning [15,16]. Core-shell upconverting nanoparticles have been shown to be a viable multimodal imaging agent since they are excited in the near infrared (NIR) region and yield emission in the visible region with comparatively better signal-to-noise ratio, low photodamage, and better penetration depth [17]. With the inclusion of Gd^{3+} and Fe^{3+} ions in the overall core structure, multimodal imaging features can be achieved [18–20]. An un-doped outer shell has even been shown to enhance the multimodal features of the core material [19]. But, one of the major issues with core-shell structured nanoparticle is the synthesis complexity and the associated cost of production.

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In order to circumvent these difficulties, a core-shell free structure was proposed where multiple functionalities can be easily achieved by doping metals with the desired properties into the same lattice. This can be easily accomplished in wide band gap materials such as oxides, halides, chalcogenides, etc. For example, trivalent rare earth metals are considered to be suitable dopants for narrow band tunable emission with a very wide range of excitation and emission in the UV–VIS–IR range [22]. Unlike QDs and organic dyes, these phosphors are free from photobleaching and do not need size control for color tunability. In addition, they have a long decay time and excellent IR absorbing features that enables imaging in the upconversion and downconversion mode. By replacing a fraction of the metal cations in the lattice with another cation having magnetic properties, a luminomagnetic nanostructures can be easily accomplished without the need of a core-shell structure. To date, several researchers have developed luminomagnetic nanocrystals (NCs) as potential multimodal imaging agents with core-shell free nanostructures [23–27].

This paper discusses the synthesis and characterization of core-shell free $Na(Gd_{0.5}Lu_{0.5})F_4:Nd^{3+}$ (NGL) as a potential NIR sensitive luminomagnetic nanophosphor for multimodal imaging application with three functionalities viz. NIR emission, X-ray fluorescence, and magnetic properties. NGL belongs to the $NaYF_4$ structure and is a wide band gap halide with an optical band gap of near 8 eV [28]. The multimodal properties of these NCs is achieved by utilizing the strong NIR fluorescence properties of the rare earth Nd^{3+}, magnetic properties of Gd^{3+}, and the high X-ray absorption properties of Gd^{3+} and Lu^{3+} in the NGL host. To the best of our knowledge, this is the first study reporting the synthesis and characterization of fully monodispersed water-soluble core-shell free nanophosphors with three imaging features.

2. Materials and methods

2.1. Synthesis

The nanocrystals were synthesized via solvothermal (ST) method using 99.9% purity precursor chemicals (GFS Chemicals, US). To make Nd^{3+} doped $Na(Gd_{0.5}Lu_{0.5})F_4$ (NGL), stoichiometric amounts of $L(NO_3)_3$ (L = Gd,Lu,Nd) and 1 g of the surfactant polyvinylpyrrolidone (PVP) were dissolved in 30 ml of ethylene glycol (Reagent, GFS Chemicals, US). The solution was then mixed with 0.21 g of sodium fluoride and 0.5 g ammonium fluoride in 20 ml of ethylene glycol. The resulting solution was heated to 200 °C for 24 h in an 80 ml stainless steel autoclave. After the reaction was completed, the nanoparticles were precipitated by adding excess ethanol and separated by centrifuging at 10,000 rpm (Z323, Labnet, U.S.) and subsequently washed 6 times with ethanol. Finally, the particles were freeze dried (25EL Freezmobile, VirTis, US) for 15 h to obtain the powder.

2.2. Phase and morphology

The X-ray powder diffraction (XRD) measurements were done with an automated diffractometer (Ultima IV, Rigaku, Japan) with Cu Kα (λ = 1.5 A) using Ni-filtered Cu Kα radiation at 44 keV and 30 mA. The data was collected in the 20°–60° range using a step size of 0.05° and a count time of 0.15 s. The particle size and morphology of the NCs were characterized by using a high resolution transmission electron microscope (HRTEM, JEOL ARM 200F) operated at 200 keV along with selected area diffraction (SAED) was used to determine the crystallinity of the samples. Electron dispersive x-ray (EDX) spectrum was obtained using a probe size of 0.13 nm and probe current 86 pA. Digital micrograph software GATAN was used for the image analyze.

2.3. Spectroscopic characterization

Optical absorption spectrum of the powder was obtained using a spectrophotometer in the scattering mode (Perkin Elmer Lambda 19, US.). Fluorescence characterization of the synthesized particles were done by exciting the sample with a near infrared (NIR) 808 nm power tunable 14-Pin butterfly module laser diode (Axcel Photonics, B2-808-3000-150) that was controlled by a laser diode driver (Throlabs LM74S2 Driver, Thorlabs Laser Diode Control LDC2000-2A) and the emission from the sample was collected by the spectrofluorimeter (Quanta Master 51,Photon Technology International Inc., US) with an InGAS detector (Teledyne Judson Technologies, 062-8451, US). Photoluminescence decay curves were measured on a Quanta Master 40 system (Photon Technology International Inc., US) using the single shot transient digitizer technique with a nitrogen laser pumped dye laser (PTI part GL-3300 + GL-302) as excitation source. The nitrogen laser has an 800 ps pulse width that pumps a high resolution dye chamber to give 525 ± 0.04 nm light. The collected decay curve was analyzed using built in software provided by PTI. For the quantum yield (QY) measurements, a barium sulfate coated integrating sphere (203 mm in diameter) (Oriel, Model 70451) was used and is mounted on the side of the spectrofluorimeter sample chamber, opposite to the excitation source. Powder sample was held in a specially designed sample holder with a quartz window to hold the powder in place and mounted at the sample port of the integrating sphere. The diffuse fluorescence spectra from the sample and the laser profile were recorded with the spectrofluorimeter by exciting the sample with an 808 nm power tunable fiber coupled Fabry Perot laser diode (Axcel Photonics, B2-808-3000-150). Fluorescence output from the sphere was collected via a liquid light guide (LLG) with a specially designed baffle that prevents the direct entry of the exciting laser beam into the detector. The LLG collects the light from the sphere and feeds to the InGAS detector through the emission monochromator. More details regarding the QY can be seen in our previous publications [29,30].

2.4. Magnetic characterization

Magnetic properties of the samples were measured using a Superconducting Quantum Interference Device (SQUID) in the Magnet and Low Temperature Facility, at Northwestern University. The hysteresis loop of magnetization at room temperature was recorded with the magnetic field sweeping from −5 to 5 T. The sample weighed was determined to be 67 mg.

2.5. X-ray excited emission

To characterize the X-ray induced luminescence or X-ray-excited scintillation (XES), the samples were irradiated in a Faxitron X-ray Cabinet System (Model RX-650). The X-ray induced luminescence was collected in a coaxial transmission irradiation configuration with the sample centered under the X-ray source. Samples were made by pressing 10 mg of the synthesized powder materials using a 7 mm diameter mold in a hand-pellet press with consistent pressure. Pellet samples were then mounted on a piece of angled teflon using double sided tape and placed ~2 mm in front of an optical fiber in the Faxitron system. The emitted light was collected with an optical fiber attached to the Edinburgh Instruments FLS920 spectrometer. All samples were excited over an X-ray range of 20–130 kVp (5 mA).

3. Results and discussions

The crystalline phase of NGL was studied using the obtained